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Short introduction to the VALSO and EXTRAVALORE project activities

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In 2009, the Italian Ministry of Agricultural and Forestry Politics (MiPAAF) financed a call of several projects on bioenergy research (DM 246/7) with the aim of stimulating the development of bioenergy production in our country. These projects regarded several aspects of bio-energy production. Among these, within thematic 3 "Valorization of by-products of the biodiesel chain", two projects were funded:

(i) "Integrated technology system for the valorization of biodiesel chain by-products (VALSO)" proposed by the Consiglio per le Ricerca e la Sperimentazione in Agricoltura (CRA), Centro di Ricerca su Colture Industriali (CRA-CIN), coordinated by Dr. Luca Lazzeri and co-cordinated by Dr. Lorenzo D'Avino;
(ii) "Development for biodiesel chain of by-product recovery (EXTRAVALORE)" proposed by the Dipartimento di Scienze Agrarie, Alimentari ed Ambientali (D3A) of the Marche Politechnic University, coordinated by Prof. Giovanni Riva and co-cordinated by Prof. Ester Foppa Pedretti.

The projects started their activities in 2010, ending in 2013 for EXTRAVALORE and in 2014 for VALSO.

1. State of the art at the beginning of the project

In 2008, Italian agriculture cultivated around 240,000 hectares with oleaginous food crops that made it possible to cover only 1/3 of the total oilseed needed for Italy's domestic food market, making it necessary to import the remaining amount from abroad (ISTAT, Cantarelli, 2007). Only a few hectares were devoted to non-food even if the transformation of oil for biodiesel production was around 450,000 t/year. This oil was almost entirely derived from the international market; more than 250,000 t came from abroad and the remaining 200,000 t were a tax-free amount that was transformed and mixed with conventional fuel (Rosa, 2007; ISPRA, 2010). If we exclude this tax-free amount, it is not possible for an Italian chain to exist at present, mainly as a consequence of the high production costs that of Italian growth oleaginous crops.

In 2009, the European biodiesel chain changed significantly as a result of the publication of Directive 28 and related acts (Transparency platform act) that outlined aims and rules for a wider diffusion of renewable energy sources in the EU, even defining a limit for the environmental sustainability of the entire biofuel chain starting from the agricultural phase (Duca et al., 2013; Soimakaillo and Koponen, 2011). These new acts for the first time proposed sustainability criteria for the definition of a virtuous fuel chain. These decisions did not succeed in stimulating the cultivation of oleaginous crops for biofuels, that in 2012 was still suffering, especially in Italy, due to its very low gross salable production if compared to other European countries. Nevertheless, in these last few years there is increasing interest for smaller pressure plants for a local chain at single farm level, to transform the oil into energy starting from local biomasses and without the technological transformation into methyl-esters, using the oil as derived from press extraction.

In any case, the valorization of biodiesel chain by-products both for large and small production plants could be a fundamental tool in opening new applicative perspectives and for the development of new non-food oleaginous crops in Italy both for energy production for biolubricants and other minor uses.

2. Organization of the two projects

2.1. VALSO project

The aim of this project was the improvement of the economic and environmental sustainability of an Italian biodiesel chain, through the recovery and the valorization of the by-products (mainly crude glycerin and defatted seed meals), by means of a biorefinery strategy in the green chemistry, as new alternative bio-based products to the conventional fossil-based materials.

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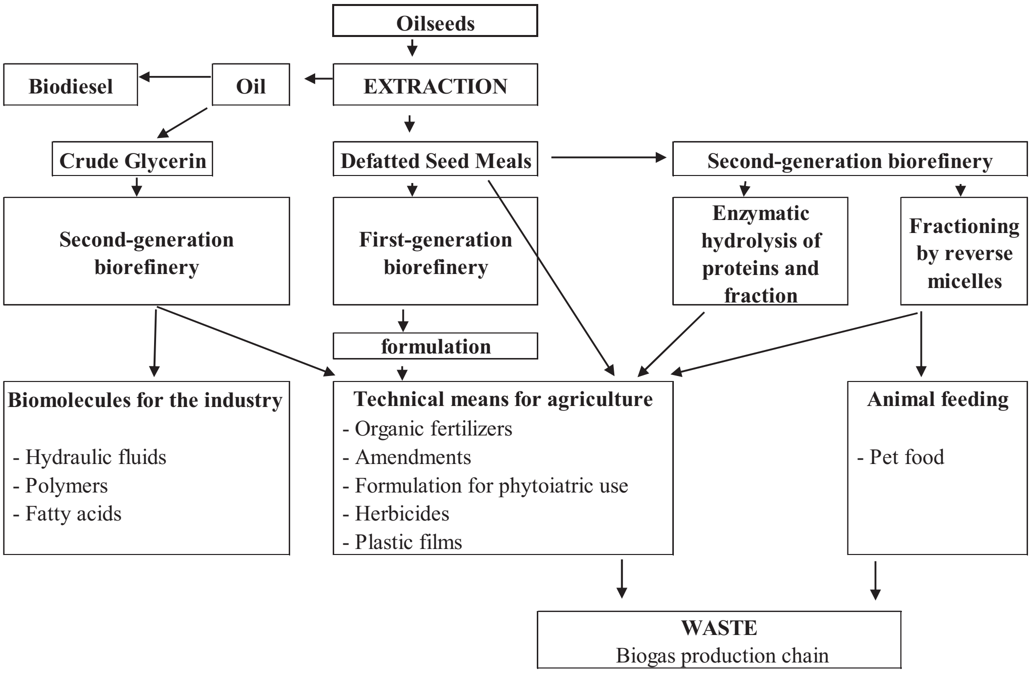
Oilseeds
EXTRACTION
Oil
Biodiesel
Crude Glycerin
Defatted Seed Meals
Second-generation biorefinery
Second-generation biorefinery
First-generation biorefinery
Enzymatic hydrolysis of proteins and fraction
Fractioning by reverse micelles
formulation
Biomolecules for the industry
- Hydraulic fluids
- Polymers
- Fatty acids
Technical means for agriculture
- Organic fertilizers
- Amendments
- Formulation for phytoiatric use
- Herbicides
- Plastic films
Animal feeding
- Pet food
WASTE
Biogas production chain

Fig. 1. Relationships among the most important Work Packages of the project, including byproducts and utilizing sectors. This flow chart of the project follows a full biorefinery approach in oil co-product valorization.

The project was organized in 4 technical Work Packages (WP) (see the Fig. 1):

1.0 Production of biomolecules for the industry (biopolymers, hydraulic fluids, coolants).
2.0 Production of technical means in agriculture (fertilizers, amendments, biostimulants, and biopesticides for the containment of pest and pathogens both at open field level and in the post-harvest phase).
3.0 Innovative processes for biomass fractionation at an industrial level.
4.0 Economic, environmental and marketing studies of the new products.

The materials studied and the proposed applications following the different production chains present in Italy can be summarized as follows:

(1) A chain based on imported oils where the industrial chain comprises high amounts of oil transformed into biodiesel and consequently high amounts of glycerin as co-product. For this application, the studies of biomolecules for the industry were proposed (WP1).
(2) A chain based on imported seeds where the industrial chain comprises oil extraction by hexane followed by oil trans-esterification. The main co-products are glycerin at a percentage of around 10% of the oil and defatted seed meals at a percentage of around 60% of the seeds. For this application, the studies of biomolecules for the industry for glycerin (WP1) and the studies on technical means in agriculture for defatted seed meals with low residual oils were proposed (WP2). This chain also benefits from the study on protein hydrolysis followed by nitrogen extraction from defatted seed meals by means of a biotechnological approach for its valorization as pet foods at high added value (WP3), using the residual biomass for energy production. The approach of using a biomass treatment for separating high added value components could be considered as a fundamental bet for a biorefinery for the future.
(3) A chain based on locally produced seeds where the industrial chain comprises oil extraction by small pressure plants. In this chain, the oil is often used as it is, directly on the farm. This chain is characterized by very small amounts of biomasses that for this reason are of little interest for large transformation plants which need homogeneous raw matter in large amounts. So, the study for these co-products has been generally limited to defatted seed meals containing oil at a percentage of around 5–10% of seed for direct application as technical means in agriculture (WP2).

The project focused its activities on co-products obtained from Italian extraction plants and, in particular, 4 different types of defatted seed meals were considered in WP2 and WP3:

(1) Conventional sunflower seeds defatted by hexane and purchased from Italcol S.p.A. Castelfiorentino (Florence, Italy)
(2) Conventional rapeseeds 00 defatted by hexane and purchased from Cerealdocks S.p:A. (Vicenza, Italy)
(3) Conventional sunflower seeds defatted by pressure and purchased from Scaramagli farm (Ferrara, Italy)
(4) *Brassica carinata* (carinata) and *Brassica nigra* (nigra) seeds defatted by a pressure plant purchased from Agrium Italia S.p.A. (Livorno, Italy)

No trials were conducted on soybean due to the almost complete absence in Italy of this crop for non-food application, and for minor new species, focusing the interest for the two more widespread oleaginous crops in Italy (sunflower and rapeseed) and a new one with an exclusive application in the non-food field (*Brassica carinata*).

For all the WP1studies, after a preliminary evaluation of the chemical characteristics of glycerin from three Italian industrial plants, the glycerin purchased from Cerealdocks S.p:A. (Vicenza, Italy) was used in the trials.

The Proposal for a COUNCIL REGULATION on the Bio-Based Industries Joint Undertaking (EU, 2013) outlined the European Bioeconomy Strategy, adopted on 13 February 2012, with the proposal of creating Public–Private Partnerships (PPP) for bio-based

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industries ("Bio-based PPP") in a full biorefinery approach. The VALSO Project tried to transpose this European approach, organizing a research partnership between private Companies, leaders in their field, and some Public Research Centres and Universities. This partnership aimed to define real innovative researches for valorization of biodiesel co-products in unusual applications different from those commercially applied for this chain (essentially in animal feeding and for energy production). In this way it was possible to identify the bio-based products that could substitute conventional fossil source chemicals, defined as emerging products in the territory due to their high impact on health and/or more generally on the environment.

The partners that collaborated in the project were as follows, reported with a short presentation of the structure and of the activities in the project.

2.1.1. *Public Research Centre*

CRA – Consiglio per la Ricerca e la sperimentazione in Agricoltura is the biggest Italian public research organization in agriculture, organized in 15 Research Centres. It participated in the VALSO project with 3 Research Centres:

CRA-CIN (*Centro di Ricerca sulle Colture Industriali*), Bologna, Italy (www.http://cin.entecra.it/). Reference people: Luca Lazzeri, Lorenzo D'Avino, Luisa Ugolini, Stefania Galletti.

CRA-CIN had considerable experience in oleaginous crops and bioactive molecules for non-food uses. The researchers of the biorefinery group of CRA-CIN played the role of coordinator of the project research activities and collaborated in almost every activity, operating at open field level in the chemical laboratory and assessing the environmental balance of each application field.

CRA-ACM (*Centro di Ricerca per l'agrumicoltura e le Colture Mediterranee*) – Acireale, Catania, Italy. (www.http://entecra.it). Reference people: Domenico Benfatto.

CRA-ACM activities were mainly related to biological control and integrated pests, pathogens and physiological disorders in citrus cultivation. The activities in the project regarded the assessment of the effectiveness of new liquid products in citrus crop protection on different pests, also evaluating biotic communities of the agroecosystems.

CRA-ORA (*Unità di Ricerca per l'orticoltura*) – Monsampolo, Ascoli Piceno, Italy. (www.http://entecra.it). Reference people: Valentino Ferrari, Enrico Piccinini.

CRA-ORA is involved in researches aimed at the selection of new horticultural varieties and at the definition of new cultivation techniques with particular emphasis on those suitable for cultivation in the middle Adriatic area and for organic farming. In this project, in the ambit of new agronomic methods with low environmental impact in horticulture, this centre studied the effectiveness of new liquid and solid (pellet) materials in pests and pathogens containment, and the fertilizing power of defatted seed meals were studied.

2.1.2. *Universities*

CSGI (Consorzio per lo Sviluppo dei Sistemi a Grande Interfase) – Sesto Fiorentino, Italy (www.csgi.unifi.it). Reference people: Alejandro Hochkoeppler, Alessandra Stefan.

The consortium has Biochemical and Molecular Biology skills for the study of proteins and enzymes and for the expression of heterologous synthetic genes in prokaryotes (*Escherichia coli*) and eukaryotes (*Saccharomyces cerevisiae*). In this project, they collaborate with CRA-CIN for the identification of appropriate enzymes and relevant biochemical parameters ensuring an efficient and inexpensive hydrolysis of proteins in defatted seed meals. Further, the production of fatty acids by the engineered oleaginous yeast *Yarrowia lipolytica* grown on glycerol culture was investigated.

DIMEVET – (*Dipartimento di Scienze Mediche Veterinarie*), Università di Bologna, www.unibo.it. Reference people: Giacomo Biagi, Carlo Pinna.

Research of DIMEVET is mainly aimed to study animal production as well as nutrition and animal feeding, including cats and dogs. In the present project, the digestibility and, in collaboration with the Dipartimento di Farmacologia of the Università di Bologna, subacute toxicity of defatted seed meals before and after enzymatic protein hydrolysis were investigated.

CiRAA – (*Centro di Ricerche Agro-Ambientali* "Enrico Avanzi"), Università di Pisa – www.avanzi.unipi.it. Reference people: Marco Mazzoncini, Daniele Antichi, Antonio Coli.

CIRAA mainly conducts on-farm research at field scale (about 120 hectares were devoted to research activity in 2012). Plot-scale experiments are usually included in the layout of larger scale (field) experiments. In the project, this centre studied the effects of the application of defatted seed meals as organic fertilizers, from the technical, economic and environmental points of view.

CRIOF – DipSA (*Dipartimento di Scienze Agrarie*) Università di Bologna, www.scienzeagrarie.unibo.it. Reference people: Marta Mari (marta.mari@unibo.it).

CRIOF – DipSA is a centre of the Agricultural Science Department of Bologna University. It is one of the main Italian centres of research involved in the study of the physiology and the protection of fruit and vegetables in the post-harvest phase. The applicative perspectives of allyl-isothiocyanate released from carinata defatted seed meals in the control of grey mould caused by *Botrytis cinerea* of strawberries and kiwifruits during storage was evaluated.

2.1.3. *Private companies and associations*

FOUNDRY CHEM, Milano (Italy). Reference people: Fiorenzo Bucelli, Gianni Rizzuto.

FOUNDRY CHEM's activity is focused on the production of lubricants and special industrial additives and the management of their application by a technical service for the users. The company thus operates in hydraulic fluids and in metalworking, generally based on renewable materials. In the project, it worked on the definition and the evaluation of new formulations based on glycerin for the sectors of hydraulic fluids sector, new specialized products for different types of processing, able to ensure best efficiency and performance combined with environmental safeguarding.

NOVAMONT SpA, Novara, (Italy) www.novamont.com: Reference people: Giulia GREGORI, Sara GUERRINI.

NOVAMONT SpA is an Italian company, pioneer in the sector of biodegradable materials, constantly devoted to the production of a new generations of products derived from renewable raw materials of agricultural origin (starches and vegetables oils). Mater-Bi® is the trade name of Novamont's the family of fully biodegradable and compostable polymers in accordance with the international norms (*e.g.*: European Norm EN 13432, "Requirements for packaging recoverable through composting and biodegradation – Testing scheme and evaluation criteria for the final acceptance of packaging"), and in different environments (compost, soil, water).

In this project, Novamont has defined an innovative raw material (granule) containing a relatively low amount of fully renewable glycerin to be filmed as mulch film. The innovative mulches were tested both at laboratory and open field levels, showing good mechanical performance and good agronomical results in open field trials.

AGRIUM SpA, Livorno (Italy). www.triumphitalia.com. Reference people: Giampiero Patalano, Elena Cheli.

AGRIUM Italia SpA is a private company involved for more than 15 years in the application of bioactive molecules for agricultural systems as a small part of a wider business in fertilizers.

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In the project, it collaborated in the definition of an industrial approach for the definition and the validation of materials for the management and the defense of horticultural crops.

PROGETTO EURO VERDE, Padova. Reference people: Stefano Bozzetto, Francesca Agostini.

PROGETTO EUROVERDE is a private company involved in organizing renewable energy chains, focused mainly on biogas and biomethane rows, followed both in their agronomic and technological phases.

In the project, it was involved in the energetic and chemical characterization and evaluation of the fibrous residues for the production of heat, of bioethanol or for utilization in biogas chain based livestock waste.

CHIMICA VERDE BIONET, Arezzo. www.chimicaverde.it. Reference people: Giuseppe CROCE, Esther SCHEMBARI, Sofia MANNELLI.

CHIMICA VERDE BIONET is a no-profit, non-political association whose bylaws include the aim of research, technological transfer and dissemination of innovation in green chemistry. In addition, it promotes the industrial and commercial phases of biobased products.

In the project, it followed the marketing evaluation for the Italian sector of the innovation derived from the project activities. It was also responsible for all the phases of dissemination of the results of the project to the industrial and agricultural sectors.

2.1.4. External collaborations

TECNOALIMENTI SpA, Milano (linked to CRA-CIN): Dr.ssa Cinzia Rebosio, Dr. Marco De Vito.

CRA-SUI (Unità di Ricerca per la suinicoltura): Dr. Rosa Marchetti.

VENETOAGRICOLTURA, Padova (linked to CRA-CIN): Dr. Lorenzo Furlan.

STUDIOSILVA, Bologna (linked to CRA-CIN): Dr.ssa Elisabetta Della Valle.

DIPARTIMENTO DI FARMACOLOGIA (linked to DIMORFIBA Università di Bologna). Dr. Andrea Sapone.

OSSERVATORIO MALATTIE DELLE PIANTE, Bologna (linked to CRA-CIN): Dr.ssa Giovanna Curto.

3. EXTRAVALORE project

The Extravalore project was focused on the potential uses of the following byproducts:

- cellulosic residues of field crops and seed processing (straw, cuticles, *etc.*);
- residues from oil extraction and refining (extraction cakes and flours, sediments, *etc.*);
- residues from the trans-esterification of vegetable oil (glycerin at different purity levels).

These byproducts can be used, partly or completely, in four different sectors, all considered to be on the same level in the Project:

- agronomic: to produce soil improvers and other similar products
- livestock: as feed
- industrial: to produce raw materials
- energy: to produce solid fuels and energy.

The first version of the project (launched in 2007) considered the oil-chains based on 3000–10,000 ha agricultural districts (“short chains”), assisted by small-sized mechanic squeezing plants that could help the local re-use of the byproducts (solution to be considered as a prospect). The traditional chain – serving larger districts with a few large oil mills (present solution) – was also included in the study. The main purpose was to improve the economic feasibility of the Italian biodiesel and bioliquid chains (vegetable oils for gen-sets and power plants in the latter case) through an extensive valorization of the byproducts (Fig. 2).

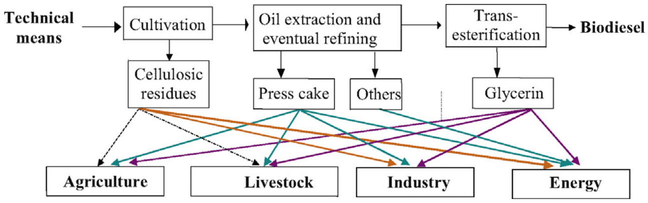

Fig. 2. Relationships among the most important elements of the biodiesel chain, byproducts and utilizing sectors. The byproducts and sectors studied by specific experimentations in this project are marked with stronger lines. Possible cellulosic residues from seed pre-processing and rubbers are included in the “other” byproducts of the extraction phase.

In the following years (2010 and later), however, the economic recovery of by-products, mainly due to the general crisis of the European markets, has been of more general interest, while the interest in domestic biofuel production (not competitive with those of importation) has decreased considerably.

The Extravalore Project was organized into six sub-projects performed by 10 different public organizations as described below.

“Raw materials” Sub-Project: CRA-CIN – Research Centre for Industrial Crops. The objective was to evaluate some of the major industrial and oil crop varieties that are best suited to the Italian environment (*i.e.*: sunflower, B. carinata, rape and thistle), to identify the most interesting cultivars in terms of production of seeds, oil, biomass. Coordinator: Dr. Andrea del Gatto.

“Economy” Sub-Project: INEA – National Institute for Agricultural Economics. The objective was to evaluate the economic viability of the short oil crop chain through: (i) assessment of the potential market of the by-products; (ii) estimation, in the medium term, of the potential contribution of by-products and derivatives to the achievement of the national target (10% incorporation of biofuels by 2020 in transport fuels). Coordinator: Dr. Annalisa Zezza.

“Agronomy” Sub-Project: CRA-ORT – Research Centre for Horticulture. The objective was to: (i) verify the technical feasibility of the use of processed flours obtained from the oil seeds as a biocide agent; (ii) verify the utilization of oil seed cakes as a soil improver/fertilizer; Coordinator: Dr. Massimo Zaccardelli.

“Livestock” Sub-Project: CRA-FLC – Research Centre for Forage and Dairy Production (reference person: Dr. Giacomo Pirlo); CRA-SUI – Research Unit for Swine Breeding (reference person: Dr. Giacinto Della Casa); CRA-PCM – Research Centre for the Production of Meat and Genetic Improvement (reference person: Dr. Miriam Del Curto); Department D3A of the Marche Polytechnic University (reference person: Prof. Federica Trombetta). The Sub-Project mainly considered the use of oil seed cake and of glycerine as feed through: (i) the characterization of the different fat cakes considered by the project and of different qualities, in terms of purity, of glycerin; (ii) several specific activities focussed on answering the following question: *is it possible to use by-products as feed materials for the production of high-quality food (meat, cheese and ham)?* General Coordinator of the Sub-Project: Dr. Giacomo Pirlo.

“Industry” Sub-Project: CHIMIND – Department of Industrial Chemistry, University of Bologna (reference person: Prof. Fabrizio Cavani); DICAM – Department of Civil, Environmental and Materials, University of Bologna (reference person: Prof. Fabio Fava), CRA-RPS – Research Centre for the Study of the Relationship between Plant and Soil (reference person: Dr. Laura Bardi). The Sub-Project considered the use of cellulosic residues and of glycerol for the production of industrial raw materials. Specific objectives: (i) development of a production process of brassinolide from field residues; (ii) development of a process of production of 1,3-propanediol from glycerol, with the design and development of a specific fixed bed

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bioreactor; (iii) development of a production process of acrylic acid from glycerol, with the design and development of a suitable bifunctional catalyst. General Coordinator: Prof. Fabrizio Cavani.

"Energy" Sub-Project: Department D3A of the Marche Polytechnic University. Objectives: (i) characterization of the most interesting by-products suitable for energy and industrial use; (ii) study of the process of oil seed decortication and of the process of mechanical oil extraction in order to optimize the quality of both the oil and the expeller (to be used as feed); study of the torrefaction and densification of the field residues (straw and cake). Coordinator: Prof. Giovanni Riva.

4. Main findings

4.1. VALSO project results

4.1.1. WP1: "biomolecules for the industry"

The use of crude glycerin as an organic substrate for a genetically modified microorganism was evaluated, in the frame of the so-called white biotechnologies. A recombinant strain of the oleaginous yeast *Yarrowia lipolytica*, containing a synthetic gene coding for a thioesterase from *Cuphea palustris* (devised for the synthesis of short-chain fatty acids) showed good adaptability to the substrate and significant, although moderate, levels of heterologous gene expression.

A granule containing a relatively low glycerin amount to be filmed as mulching plastic with improved renewability, was defined and produced (Scarascia-Mugnozza et al., 2006). The produced materials were tested both at laboratory and open field levels, showing good mechanical performances and good results at open field level, determining interesting environmental perspectives (Razza et al., 2010).

A non-flammable hydraulic fluid was formulated, characterized by ISO 46 viscosity in which the conventional synthetic glycerin and glycol were totally substituted, obtaining industrial performances similar to conventional products (Winter et al., 2012). The formulation is based on a mixture of polymers and biopolymers, and it is glycol-free (monoethylenic, diethylenic and others). Compared to traditional water/glycol based HFC hydraulic fluid, the product allows easy disposal of the exhausted fluid and environmental safety.

Some preliminary experiences on the potential pelletizing properties of crude glycerin did not provide the expected results. Other studies are still in progress.

4.1.2. WP2: technical means in agriculture

Definition of a technological hydrolysis process of defatted seed meal proteins for the production of a hydrolysate rich in free amino acids (Adler-Nissen, 1986), small peptides and other bioactive compounds with potential biostimulant properties. Biostimulant activity was tested in *in vitro* and *in vivo* assays and showed interesting effect on plant root development (Audus, 1972). This procedure for biomass fractioning and valorization also produced residual wet meal containing a lower nitrogen content that can be exploited to produce biogas for energy source by anaerobic digestion.

Evaluation in different experiences, on fertilizing and amending effect of different defatted seed meals and on defatting procedures by microcosm, lysimeter trials and in open field on tomato and melon. Lettuce, chard and spinach productivity was analyzed in relation to the application of different defatted seed meals as fertilizers using a lysimeter batch in order to evaluate potential nitrogen leaching (Mazzoncini et al., 2005). Defatted seed meal soil incorporation in addition to a good fertilizing effect of nitrogen and carbon level stimulates microbial activities, improving biological fertility and significantly reducing nitrogen leaching.

Evaluation at pot level of the efficacy of defatted and formulated seed meals from *B. carinata* selected varieties in the control of the nematode *Meloidogyne incognita* (Lazzeri et al., 2011). The formulation aimed to modulate, over time, the release of biologically active molecules playing a fundamental role in the efficacy and repeatability of the treatment. A study on the evolution of microorganisms in the soil by molecular techniques revealed a different impact and resilience of the system in the thesis with defatted seed meals. Other trials on fungi (*Acremonium cucurbitacearum* and *Monosporascus cannonballus*) showed a clear biostimulant effect of meals especially if applied together with *T. harzianum* (Galletti et al., 2008).

Definition of pre-pilot plant for the application of allylisothiocyanate from carinata defatted seed meals in controlling some post-harvest pathogens such as *Botrytis cinerea* on strawberry and actinidia fruits (Mari et al., 2002). Treatments showed to reduce the incidence of post-harvest grey mould on naturally infected strawberry, while unclear results were obtained in artificially inoculated actinidia (still under investigation). Low Allylisothiocyanate residues were found on fruit and no influence on antioxidant capacity determined on treated strawberries was registered. Some other experiments were carried out on rice seeds for Fusarium containment and on potatoes to test the antigerminative potential of the treatment. Positive results were obtained with rice, while some difficulties were encountered with potatoes, confirming the promising feasibility of the technique but also the need for further studies in this field.

Definition and improvement of some liquid formulations based on an oil/water emulsion that contains biofumigant defatted seed meals (Rongai et al., 2006). Even if this use comprises the use of both oil and meals, this application could open new perspectives for an alternative use of *B. carinata* biomasses that could permit a wide production of biomass partially used in biodiesel or biolubricant chain and partially in liquid formulations with an improved added value. These liquid formulations have shown a clear containment of several Citrus epigeous pests and a reduction of damaged plants statistically not different from the conventional products for the powdery mildew control on melon or red spider mite on eggplant and of black aphid on artichoke.

A synergic activity of crude glycerin and biofumigant defatted seed meal in seed germination inhibition was also shown both *in vitro* and *in vivo* trials, opening interesting perspectives in the definition of a non-chemical alternative in organic weed control (Dayan et al., 2009).

4.1.3. WP3: innovative processes for biomass fractionation at an industrial level

Evaluation of an extraction system based on reverse micelle (Ugolini et al., 2008), based on the use of a solution of water and an apolar solvent with the addition of a non-ionic surfactant for a separation of polar compounds in the water fraction and of the oil in the apolar fraction. The system confirmed several limits of recovery of the different compounds that make real application possible only in the long term after several other studies aimed at finding low impact additives and surfactants.

Definition of a second procedure of defatted seed meal hydrolysis to obtain a technical hydrolysate containing a significant amount of dipeptides to be used as a pet food component. The evaluation of the main chemical and nutritional characteristics of hydrolysates was pursued with studies on their digestibility and toxicology in rats.

Evaluation of the potential application of ultrafiltration for separating protein hydrolysates and the application of spray dried technique as a system of concentrating water soluble compounds. Even if the studies did not furnish applicative innovation, the topic of considering fractionation systems of biomasses will play a fundamental role in the valorization of biomasses of low added values, reserving an application for bioenergy production only to the residual materials.

A first experiment in this direction was performed in the study of the fibrous residues after protein removal from sunflower and rapeseed defatted seed meals for their calorific power and methanogenic power in biogas chain.

4.1.4. WP4 economic, environmental and marketing evaluation of the main innovative products

Definition of a methodology for assessing the new products obtained from defatted oilseed meals and/or crude glycerin was carried out. This assessment was possible only for products that go beyond at least the laboratory level and was significant in relation to Technology Readiness Levels. At the beginning of the project, twenty different products were potentially identified; about half of these, however, could pass from scientific hypotheses beyond laboratory level, demonstrating technical feasibility at pilot level, using breadboard or brassboard implementations. In fact, some hypotheses were wrong, *e.g.* the use of certain meals as early drop agents, or, in other cases, the industrial application was linked to non-solvable problems, *e.g.* the increase in mould after the application of crude glycerin as an anti-sprouting agent in potato post-harvest treatment. The best innovative products that were obtained and evaluated by market analyses and environmental assessment were presented in this special issue.

First of all, it was necessary to identify the conventional homologous products taking into account the power of substitution with similar capabilities. For bio-based products this is not an easy step, because several different types of replacement can occur.

In some cases, the application of a bio-based product can replace the use of a conventional product (the homologous one); this was the case *e.g.* of substitution of synthetic glycerol with crude glycerin in biodegradable mulching film formulation. In other case the biobased product can replace more than one product, for example in the biofumigation technique, formulated meals contained soil borne pests and pathogens (even though with different efficacy as regards chemical fumigants), but, at the same time, the organic nitrogen contained in meals made it possible to avoid the use of synthetic nitrogen in horticulture pre-transplant applications, increasing the economic and environmental benefit derived from the replacement. In other cases, several bio-based products were necessary to replace a single conventional product; this is the case of the synergistic effect of glycerin and meals in limiting weeds.

In any case, the replacement could provide several environmental benefits that it is not always possible to quantify. So, our objective was to quantify the replacement effect, focusing on the main sustainability criteria, well aware that the assessment may not be exhaustive.

Briefly, the economic assessment was aimed at identifying the conventional (non-biobased) products on the market, evaluating the size of this market, focussing mainly oriented on the Italian market.

The environmental assessment criteria (Spugnoli et al., 2012) involved the source, the processes and the destination of innovative biobased products: (i) the increase in renewability, as renewable carbon content, compared with conventional homologous products, (ii) the carbon footprint, by life cycle assessment methodology, allocating common greenhouse gas emissions to different co-products on an economic basis or expanding the system boundaries by the substitution method, (iii) the environmental fate of different products, highlighting benefits in possible reduction of waste toxicity or benefits when directly released into the environment.

4.2. Short conclusions

A general overview on the results of the project shows how national biodiesel or biolubricant chains could benefit from a real valorization of residues and especially byproducts of oil extraction in high added value fields of application. The explored applications in the production of biomolecules for industries and of technical means for agriculture today represent a real urgent option considering the problems for health and for the environment caused by conventional chemical application. The perspective of fractioning the by-product can permit the separation of high added molecules as seen for hydrolysates, permitting the preparation of several materials with different applications, an approach that is fundamental for every innovative biorefinery.

Evaluation of the environmental balance and of potential market interest is an aspect that represents an important added value to the project activities.

4.3. EXTRAVALORE project results

The name of the Extravalore Project ("Extra-value") underlines the possibility to valorize the currently unexpressed or very low economic value of byproducts: the project examined the biodiesel chain, but it also highlighted, in more general terms, the opportunities offered by the re-use of the byproducts of different agricultural chains. As a consequence, the results are significant not only in relation to the biofuel chains but also provide interesting information that is useful in general terms.

In the agronomic sub-project, the use of seed flours and cakes of *Brassica carinata* and rape was tested for use as biocides the first case and as soil conditioners in the latter. In detail, the tests have shown the reducing action of the flours of *Brassica carinata*, in association with bacterial strains fungicides and essential oils, against fungal attacks to vegetables. This makes it possible to produce low impact fungicides that could replace banned or unsustainable chemical compounds. The brassica and rape cakes made it possible, with their soil conditioner action, to improve vegetable production in the field and increased the soil quality in terms of additional organic carbon (Raccuia et al., 2013).

In the livestock sub-project, the cakes produced by the mechanical extraction of oil from sunflower whole or de-hulled seeds and the glycerin coming from the transformation of the vegetable oil into biodiesel have were used as feed. The experiments on different groups of cattle and pigs confirmed the technical feasibility to substitute and to reduce the imports (in the Italian context) of soy bean flour making it possible to establish alternative traceable feed chains that could give and extra-value to local food products. Cakes and glycerin were used to feed dairy cattle, beef cattle and pigs to be transformed into fresh high quality products, such as premium milk, meat and ham. In comparison with the traditional feed, cakes and glycerin did not change the production performances and have also showed the possibility of reducing the costs of the feed ration (Abeni et al., 2012; Cabassi et al., 2013; Della Casa et al., 2009; Povolo et al., 2012).

The industrial sector has a very large potential in terms of vegetable by-products transformation (bio-refineries). In the industry sub-project two innovative processes have been studied: the biochemical conversion of raw glycerin into 1,3-propanediol and the chemical conversion of the pure glycerin into acrylic acid, by a specific catalyst. In addition, the field residues of rape and *Brassica carinata* (straw) could be processed to enhance their yields of the phytohormones that could be used for crop protection (Casali et al., 2012; Chieregato et al., 2012).

In the energy sub-project, a database of chemical/physical properties of all considered by-products has been created to make possible the evaluation of the technical feasibility of their re-use.

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The study has also identified strengths and difficulties of the energy transformation by thermo/chemical or biological processes. In particular, the problems related to the low energy density and to the instability over time of the characteristics of the field residues (straw and stalks) and residues from the first transformation (cakes) from sunflower, rape and *Brassica carinata* have been studied. The examined solutions were densification (by pelletizing and briquetting) and torrefaction (by reactors not in pressure; Riva et al., 2013).

Among the results of the project, it's to be highlighted the lot of information obtained from the agronomic tests on the production of sunflower, rape and *Brassica carinata* verifying the suitability to the national environment of some specific varieties and their responses – in terms of seeds, oil concentration and field residues production – at different levels of the most important production inputs.

The agronomic tests showed the need of a constant updating – in terms of adaptability and productivity – of the different cultivars to the Italian climatic conditions and to the different technical itineraries and the need of further details on the reactions of rape and sunflower to nitrogenous fertilizers: all that with the goal of finding the most convenient level of the fertilizer quantity (Pane et al., 2012).

4.4. Short conclusions

A general overview on the results of the project shows that the national biodiesel chain could find and maintain its role by a re-use of its byproducts. This conclusion can be considered valid also for many other national chains, food and innovative included, at present less convenient than in the past. For example, the use of the cake from partially peeled sunflower seeds, for pig fattening appears to be very interesting. In fact, it is possible, with low investments, to set up a new chain based on the cultivation of sunflower, partly sheltered from the world market price variations, and able to control the inputs and the utilized technologies. The high production of integuments, from the treatment of the sunflower seeds and the field residues, gives the opportunity of producing thermal energy for different uses.

It is clear that these kinds of solutions are based on a strong integration of the different rural activities that are not easy to realize at present.

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